



# Quantitative studies on thermal stability of a FeF<sub>3</sub> cathode in methyl difluoroacetate-based electrolyte for Li-ion batteries



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## HIGHLIGHTS

- The thermal behavior of FeF<sub>3</sub> was investigated in MFA-based electrolyte.
- MFA-based electrolyte showed great thermal stability up to 500 °C.
- The cycled FeF<sub>3</sub> cathodes were reacted with MFA electrolyte at high temperatures.
- The safety of FeF<sub>3</sub> battery was improved by using MFA-based electrolyte.

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## ABSTRACT

The thermal behaviors of FeF<sub>3</sub> cathode in 1 mol dm<sup>-3</sup> LiPF<sub>6</sub>/methyl difluoroacetate (MFA) electrolyte are quantitatively investigated by differential scanning calorimetry. MFA-based electrolyte shows great thermal stability without heat generation up to 500 °C. The cycled electrodes are studied and find to become more thermally stable after lithiation. Furthermore, the lithiated electrode shows a superior thermal stability in the electrolyte compared to the delithiated electrode. Although the heat generated by the mixtures of cycled electrodes and MFA-based electrolyte is larger, the lithiated and delithiated electrodes coexisted with MFA-based electrolyte are about 140 and 230 °C higher than that of EC + DMC-based electrolyte, respectively. Therefore, the safety of FeF<sub>3</sub> battery is enhanced by using MFA-based electrolyte instead of EC + DMC-based electrolyte.

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## 1. Introduction

Rechargeable lithium-ion batteries are the most promising candidates for applications in hybrid electric vehicles (HEVs) and electric vehicles (EVs), due to their high energy density and power density. However, many Li-ion batteries explosion accidents have been reported, which bring out more and more serious concerns on the safety of batteries. The safety of Li-ion batteries is mainly related to the thermal stability of their constituent materials [1–6]. Exothermic reactions such as the reaction between electrolyte and electrode and the decomposition of electrolyte in the battery can cause thermal runaway at elevated temperatures. To enhance the battery safety, it is important to clarify the factors of thermal risk for Li-ion batteries.

Recently, metal fluorides such as FeF<sub>3</sub>, VF<sub>3</sub>, CoF<sub>2</sub> and NiF<sub>2</sub> have been studied as optional candidates for cathode materials for Li-ion batteries [7–14]. Among them, FeF<sub>3</sub> has become one of the most promising cathode materials because of its large theoretical capacity and high discharge voltage. However, FeF<sub>3</sub> delivered a relatively low capacity of 80 mAh g<sup>-1</sup> due to its poor electronic conductivity [10]. By using highly conductive carbon, the electrochemical activity was improved, and a good reversible behavior of about 230 mAh g<sup>-1</sup> has been achieved for FeF<sub>3</sub> cathodes [11,12]. Moreover, the reversible conversion reaction of FeF<sub>3</sub> was enabled, and high capacities (>600 mAh g<sup>-1</sup>) are accessible at room temperature [15,16]. Due to the outstanding improvement of the electrochemical performance, FeF<sub>3</sub> becomes an attractive cathode material for vehicle power supply. From the point of practical application, the thermal stability of FeF<sub>3</sub> cathode must be studied because it is crucial for the battery safety. Our group previously investigated the thermal stability of FeF<sub>3</sub> cathode in EC + DMC-based electrolyte and found that the exothermic heats are mainly

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caused by the thermal decomposition of electrolyte [3]. To optimize the safety of  $\text{FeF}_3$  battery, an electrolyte with great thermal stability is needed.

Many of fluorinated organic solvents have been studied as co-solvents of electrolytes to enhance the thermal stability of Li-ion batteries due to their excellent nonflammability. The thermal stability of partially fluorinated carboxylic esters as electrolyte solvents was investigated. From the study, methyl difluoroacetate (MFA)-based electrolyte containing  $\text{LiPF}_6$  exhibits better thermal stability in coexistence with lithium metal or graphite anode than that of conventional electrolytes such as an EC + DMC-based electrolyte [17–19]. Additionally, the  $1 \text{ mol dm}^{-3}$   $\text{LiPF}_6/\text{MFA}$  electrolyte with delithiated  $\text{Li}_x\text{CoO}_2$  also was proved to have better thermal stability than an EC + DMC-based electrolyte [20].

In this work,  $\text{FeF}_3$  was applied as the active cathodic material in Li-ion batteries. By changing the ratio of cycled electrodes to electrolyte, the thermal behaviors of  $\text{FeF}_3$  electrode in MFA-based electrolyte were quantitatively studied by DSC.

## 2. Experimental

Commercially available  $\text{FeF}_3$  (Soekawa Chemical Co.) was used in this research. The cathode was prepared by using the  $\text{FeF}_3$ , acetylene black and PTFE-binder (70:25:5 wt%). The fabrication method of pellets and cell construction were the same as described in the experimental sections of Ref. [3].  $1 \text{ mol dm}^{-3}$   $\text{LiPF}_6$  was dissolved in MFA (Daikin Fine Chemical Co. Ltd.) to prepare the electrolyte used in this study. The cell was cycled between 2.0 and 4.5 V at a constant current density of  $0.2 \text{ mA cm}^{-2}$ . After the third charging or discharging, the coin cell was disassembled in the glove box to take out the cathode. The electrode was rinsed and soaked in MFA solvent for 4 h, and then vacuum-dried under vacuum at room temperature for 12 h to remove low-molecular weight compounds. A given amount of the electrode powder together with electrolyte was packed in a crimp-sealed stainless pan. The thermal properties were investigated by TG-DSC at a heating rate of  $5^\circ\text{C min}^{-1}$  from room temperature to  $500^\circ\text{C}$ . No leakage was verified by the absence of weight loss in TG curves during heating.

## 3. Results and discussion

The charge/discharge profile of  $\text{FeF}_3$  electrode in  $1 \text{ mol dm}^{-3}$   $\text{LiPF}_6/\text{MFA}$  electrolyte is shown in Fig. 1. The initial discharge and charge capacities were 232 and  $202 \text{ mAh g}^{-1}$ , respectively. Hence, the irreversible capacity in the first cycle for  $\text{FeF}_3$  was  $30 \text{ mAh g}^{-1}$ . After the second cycle, the charge and discharge reaction proceeded reversibly and the irreversible capacity was negligibly small. The  $\text{FeF}_3$  showed the similar electrochemical properties in MFA-based electrolyte as that in EC + DMC-based electrolyte [3,12].

Fig. 2 shows DSC curves of 1 mg  $\text{LiPF}_6$  salt, 2  $\mu\text{l}$  MFA solvent and 2  $\mu\text{l}$  of 1 M  $\text{LiPF}_6/\text{MFA}$  electrolyte. When 1 mg  $\text{LiPF}_6$  salt was sealed in a hermetic pan, a broad endothermic peak was observed at temperatures ranging from  $240$  to  $310^\circ\text{C}$  followed by a small endothermic peak at around  $200^\circ\text{C}$ . The large endothermic peak in the range of  $240$ – $310^\circ\text{C}$  should be attributed to the decomposition of  $\text{LiPF}_6$  ( $\text{LiPF}_6(\text{s}) \leftrightarrow \text{LiF}(\text{s}) + \text{PF}_5(\text{g})$ ) after it melted at about  $200^\circ\text{C}$  [21]. On the other hand, a small endothermic peak due to the evaporation of MFA solvent was seen at about  $220^\circ\text{C}$ , while exothermic peaks appeared at above  $460^\circ\text{C}$  just after the MFA solvent gasified. However, when 2  $\mu\text{l}$  of MFA-based electrolyte containing  $\text{LiPF}_6$  was investigated, only two endothermic peaks were observed up to  $500^\circ\text{C}$ ; a peak at around  $220^\circ\text{C}$  was due to the evaporation of MFA solvent, the other peak at about  $240^\circ\text{C}$  could be

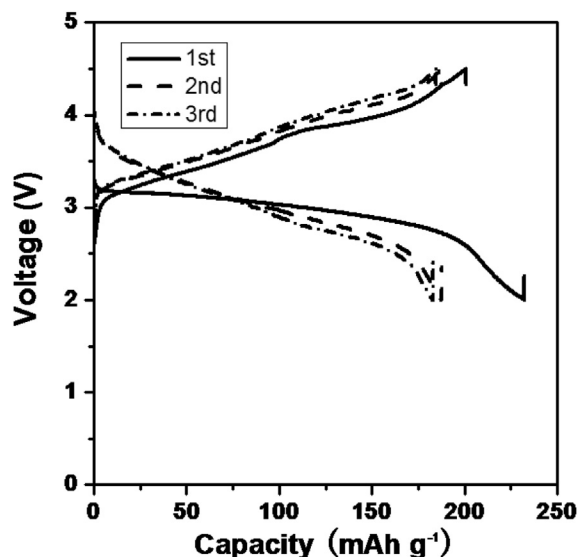


Fig. 1. The cycling profiles of  $\text{FeF}_3$  electrode in 1 M  $\text{LiPF}_6/\text{MFA}$  electrolyte.

attributed to the decomposition of  $\text{LiPF}_6$  salt [22]. We previously reported that a large exothermic peak was observed at around  $270^\circ\text{C}$  for  $1 \text{ mol dm}^{-3}$   $\text{LiPF}_6/\text{EC} + \text{DMC}$  electrolyte due to its self-decomposition [1,3]. These results suggest that an MFA-based electrolyte had better thermal stability than an EC + DMC-based electrolyte when  $1 \text{ mol dm}^{-3}$   $\text{LiPF}_6$  was used as the salt. Although the detailed mechanism has not been clarified yet, the high thermal stability of a MFA-based electrolyte seems to be contributed by a strong Lewis acid of  $\text{PF}_5$  in the electrolyte, which is the product of  $\text{LiPF}_6$ . The Lewis acid attacks a lone pair of electrons on an oxygen atom in MFA molecules. As a result, the electron density of  $\text{PF}_5$  would decrease in MFA, which leads to a decrease in its reactivity, resulting in suppressing the exothermic reactions in MFA-based electrolyte [20].

To study the thermal stability of a cycled electrode in absence of electrolyte, 8 mg of cycled electrode powder was sealed in a stainless-steel pan for DSC analysis. The results are shown in Fig. 3.

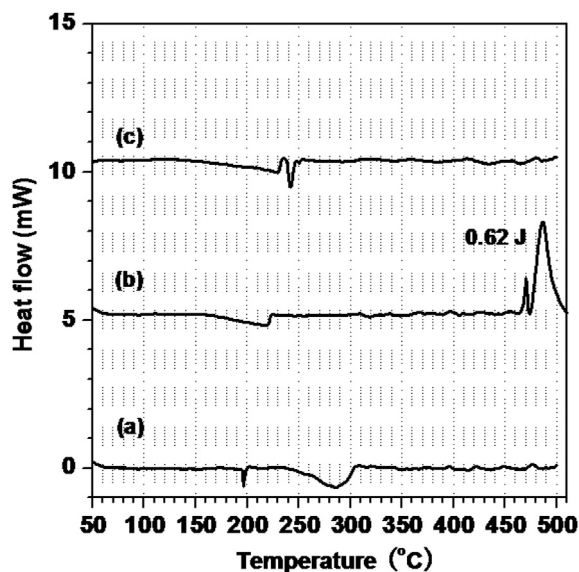


Fig. 2. DSC curves of (a) 1 mg  $\text{LiPF}_6$ , (b) 2  $\mu\text{l}$  of MFA solvent, and (c) 2  $\mu\text{l}$  of 1 M  $\text{LiPF}_6/\text{MFA}$  electrolyte.

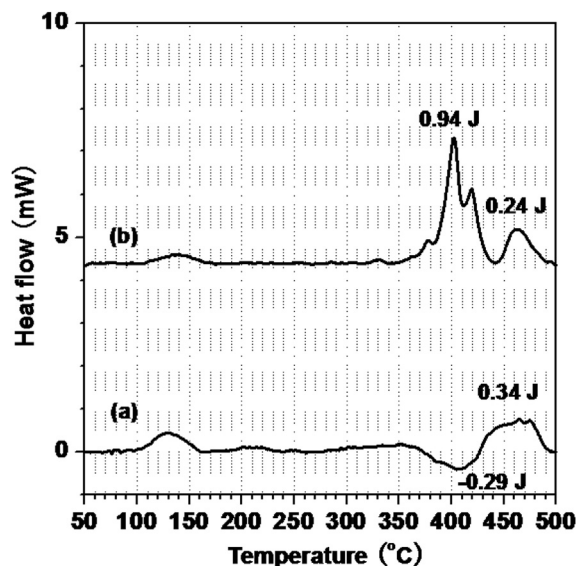


Fig. 3. DSC curves of 8 mg: (a) lithiated  $\text{FeF}_3$  electrode powder after 2.5 cycles, (b) delithiated  $\text{FeF}_3$  electrode powder after 3.0 cycles.

A broad peak at around 100–160 °C was observed for both lithiated and delithiated  $\text{FeF}_3$  electrodes, which has been identified as the decomposition of the surface film formed on the electrodes during the cycling [3]. The difference of thermal behaviors between the lithiated and delithiated electrodes was distinct. The delithiated electrode gave exothermic peaks at temperatures in the range of 340–500 °C. However, in the same temperature range, small endothermic and exothermic peaks were observed for the lithiated electrode. Obviously, heat generation due to self-decomposition from the lithiated electrode was milder than the delithiated one. Hence, the thermal risk of  $\text{FeF}_3$  electrodes became much lower after lithiation. Compared to the electrodes obtained for EC + DMC-based electrolyte [3], the thermal behaviors of both lithiated and delithiated electrodes were quite similar, indicating that similar lithiation/delithiation reactions occurred for  $\text{FeF}_3$  electrodes in these electrolytes.

From the point of practical applications, heat generation caused by the reaction of lithiated/delithiated electrodes and electrolyte is crucial for the battery safety. Thus, the thermal behavior of lithiated and delithiated  $\text{FeF}_3$  electrodes in MFA-based electrolyte was investigated in detail by DSC measurements.

Fig. 4 shows DSC curves of mixtures of 1 mg lithiated electrode and given amounts of the electrolyte ranging from 0.5 to 2  $\mu\text{L}$ . When the amount of electrolyte was 0.5  $\mu\text{L}$ , heat generation was observed at temperatures started from 350 with the peak at around 430 °C, and the heat value was evaluated to be 0.99 J. With the addition of electrolyte from 0.5 to 1  $\mu\text{L}$ , the exothermic heat at around 430 °C increased gradually. This phenomenon suggests that the electrolyte was involved as one reactant. The other reactant was supposed to be the lithiated electrode, because the lithiated electrode was decomposed at this temperature range, together with endothermic and exothermic peaks (Fig. 3a). Thus, the exothermic peak at around 430 °C could be assigned to both the reaction of lithiated electrode with electrolyte and the self-decomposition of electrode. When the coexisting electrolyte was added to 2  $\mu\text{L}$ , the exothermic peak at about 430 °C further increased. Together with that, a new exothermic peak at about 470 °C became dominant and partially overlapped with the peak of 430 °C, and its heat value was much larger than that as expected. When the amount of electrolyte was excess, a part of electrolyte was reacted with lithiated electrode at

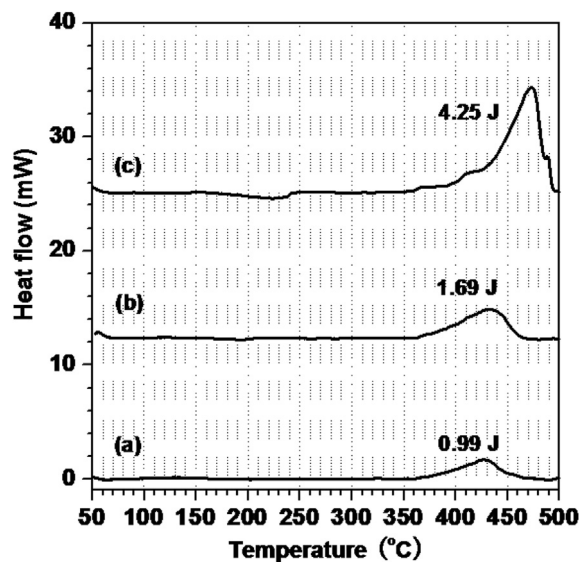


Fig. 4. DSC curves of mixtures of (a) 0.5  $\mu\text{L}$ , (b) 1  $\mu\text{L}$ , and (c) 2  $\mu\text{L}$  MFA-based electrolyte and 1 mg lithiated  $\text{FeF}_3$  electrode powder after 2.5 cycles.

around 430 °C. After that, the remaining electrolyte was consumed by further thermal reaction with the products of the reaction between lithiated electrode and electrolyte, which was corresponding to the exothermic heat at around 470 °C.

Fig. 5 shows DSC curves of mixtures of 1  $\mu\text{L}$  electrolyte and given amounts of lithiated electrode (ranging from 1 to 3 mg). When the coexisting electrode was 1 mg, an exothermic peak was observed at around 430 °C. With the increasing of lithiated electrode, the exothermic peak at around 100–160 °C due to decomposition of the surface film also increased gradually (see the insert in Fig. 5). At the same time, the dominant exothermic peak slightly shifted to lower temperature of 410 °C, and their heat values decreased with the addition of lithiated electrode. Other than that, when the amount of coexisting electrode was 3 mg, a small exothermic peak between 450 and 490 °C was observed, which could be due to the self-decomposition of the lithiated electrode (Fig. 3a). Obviously,

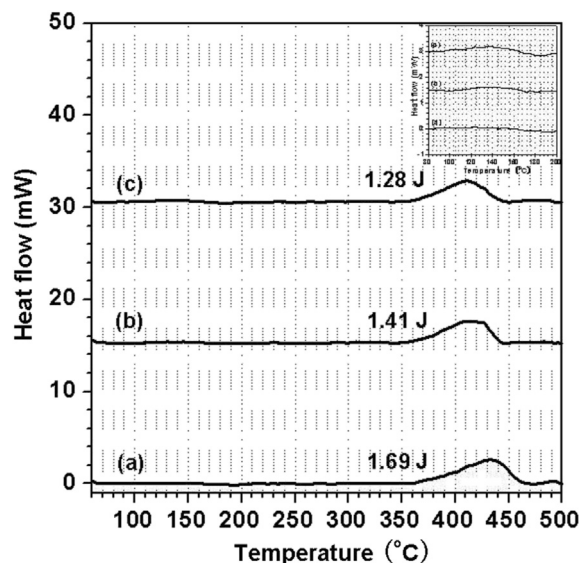
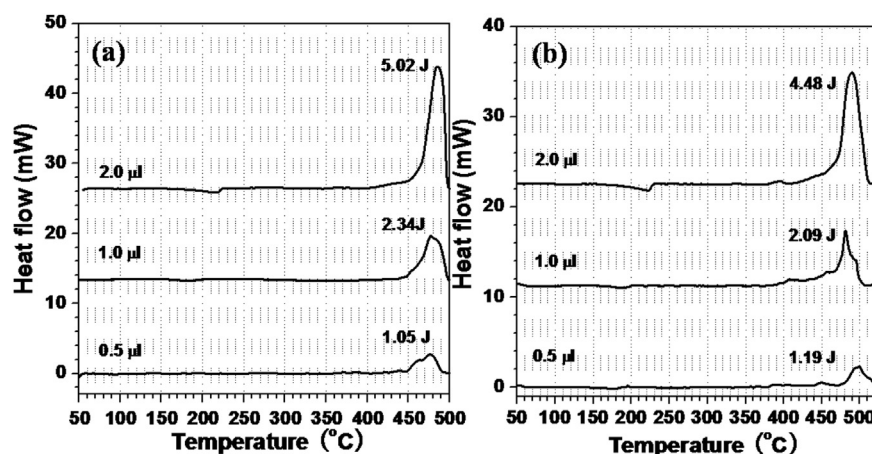


Fig. 5. DSC curves of mixtures of 1  $\mu\text{L}$  MFA-based electrolyte and (a) 1 mg, (b) 2 mg, and (c) 3 mg lithiated  $\text{FeF}_3$  electrode powder after 2.5 cycles.



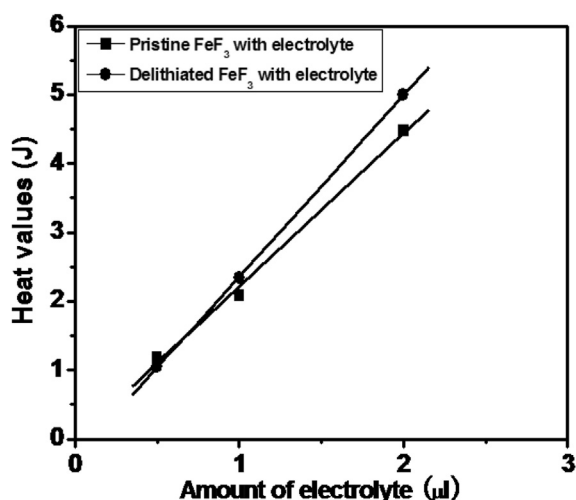
**Fig. 6.** DSC curves of (a) mixtures of 0.5  $\mu\text{l}$ , 1  $\mu\text{l}$ , and 2  $\mu\text{l}$  MFA-based electrolyte with 1 mg delithiated  $\text{FeF}_3$  electrode powder after 3.0 cycles; (b) mixtures of 0.5  $\mu\text{l}$ , 1  $\mu\text{l}$ , and 2  $\mu\text{l}$  MFA-based electrolyte with 1 mg pristine  $\text{FeF}_3$  powder.

the dominant exothermic peak was limited by the amount of electrolyte when the coexisting electrode was above 1 mg. The amount of electrolyte was not sufficient, and some amount of electrode remained from the reaction with electrolyte. The decomposition of lithiated electrode occurred instead of the exothermic reaction between the electrolyte and the products of the reaction between electrolyte and electrode. Furthermore, the lithiated electrode due to self-decomposition gave an endothermic peak at temperatures ranging from 360 to 430  $^{\circ}\text{C}$  (Fig. 3a). As a result, the heat generation from the mixture of lithiated electrode and electrolyte decreased with the addition of the coexisting electrode.

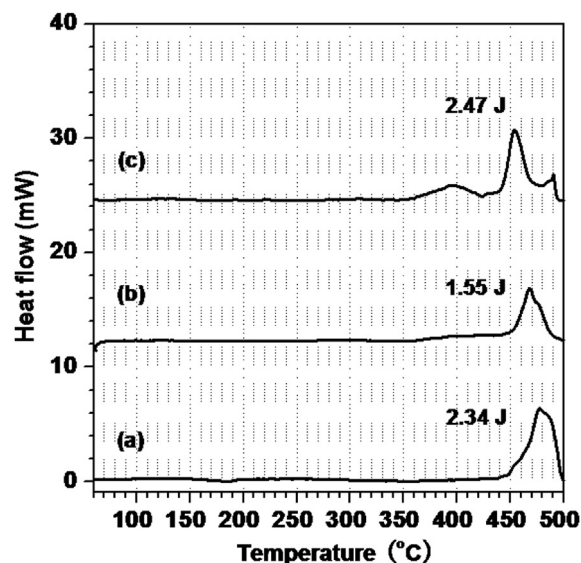
Fig. 6a shows the variations in DSC curves for mixtures of 1.0 mg delithiated electrode powder and given amounts of MFA-based electrolyte. When the amount of coexisting electrolyte increased from 0.5 to 2  $\mu\text{l}$ , a dominant exothermic peak appeared at about 480  $^{\circ}\text{C}$ , and the heat values increased significantly. Such large heat generation did not occur for neither MFA-based electrolyte nor the delithiated electrode only (Figs. 2 and 3). Thus, the exothermic heat should be closely related to both the delithiated electrode and electrolyte. On the other hand, thermal behavior of pristine  $\text{FeF}_3$  in MFA-based electrolyte was investigated by DSC, as shown in Fig. 6b. Exothermic reactions occurring at around 480  $^{\circ}\text{C}$  were also seen for

the mixtures of pristine  $\text{FeF}_3$  and electrolyte, while the pristine  $\text{FeF}_3$  was extremely thermally stable at elevated temperatures [3]. Further, the thermal behaviors were quite similar to those of the delithiated electrode coexisting with the electrolyte. Therefore, the exothermic peaks at around 480  $^{\circ}\text{C}$  in Fig. 6a were mainly caused by the reaction of  $\text{FeF}_3$  with the electrolyte, but the observed difference may have been due to a part of irreversible  $\text{LiFeF}_3$  and/or the other composites in the electrode. This assumption can be further examined by a detailed analysis of the heat values. Fig. 7 shows the correlation between the heat values and the amount of electrolyte in Fig. 6. The heat values increased in proportion to the amount of electrolyte in both cases. Linear fitting was carried out by the least-squares method, but the slope of line related to delithiated electrode was much larger. These results support the above assumption. Besides the main reaction between  $\text{FeF}_3$  and electrolyte, other reactions were thought to happen for the delithiated electrodes in the electrolyte.

Fig. 8 shows DSC curves of 1  $\mu\text{l}$  electrolyte with given amounts of delithiated electrode powder (ranging from 1 to 3 mg). When the coexisting electrode was 1 mg, an exothermic peak was observed at



**Fig. 7.** Correlation between the heat values and the amount of electrolyte in Fig. 6.



**Fig. 8.** DSC curves of mixtures of 1  $\mu\text{l}$  MFA-based electrolyte and (a) 1 mg, (b) 2 mg, and (c) 3 mg delithiated  $\text{FeF}_3$  electrode powder after 3.0 cycles.



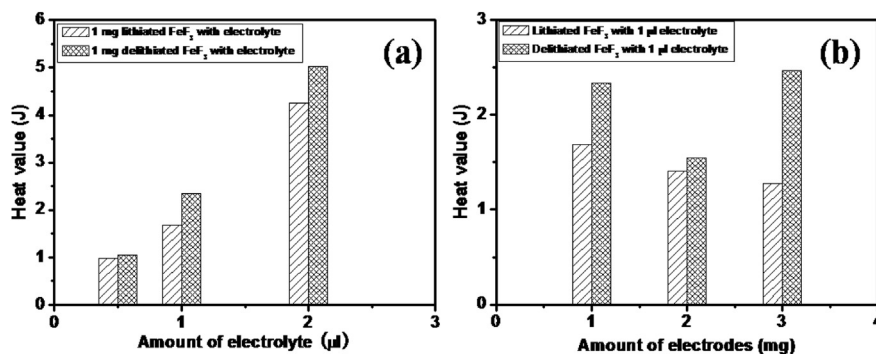


Fig. 9. Comparison of the heat values for the lithiated/delithiated FeF<sub>3</sub> electrodes in the MFA-based electrolyte.

480 °C with the heat value of 2.34 J. With a further increase of electrode from 1 to 2 and 3 mg, the dominant peak finally shifted downwards to 455 °C, and the heat values were evaluated to be 1.55 and 2.47 J, respectively. These results suggest that the heat generation due to the reaction between FeF<sub>3</sub> and electrolyte was depended on the ratios of electrolyte to electrode. Other than that, a new exothermic peak at temperatures in the range of 350–430 °C appeared and gradually increased. In this range, an exothermic peak also was found in DSC curves for the mixtures of lithiated electrode and electrolyte (Fig. 5). Moreover, some of Li-ions was still trapped in delithiated electrode, especially for the initial cycle, as shown in Fig. 1. Hence, the exothermic peak ranging from 350 to 430 °C could be assigned to the reaction between the irreversible LiFeF<sub>3</sub> and electrolyte, which is agreed well with the discussion for Fig. 6. At the same time, when the coexisting electrode was 3 mg, a small exothermic peak at about 490 °C should be noticed, which might be attributed to the thermal decomposition of the products of the reaction between the FeF<sub>3</sub> and electrolyte.

The heat generation from the mixtures of lithiated and delithiated FeF<sub>3</sub> electrodes and electrolyte was compared, and the heat values were evaluated by integrating the DSC curves in the range of 350–500 °C. As described above, dominant exothermic peaks in all cases were observed in this range. The heat values of the mixtures of 1 mg lithiated/delithiated FeF<sub>3</sub> electrodes and given amounts of electrolyte are shown in Fig. 9a, while the heat values of the mixtures of 1 μl electrolyte and given amounts of lithiated/delithiated electrodes are shown in Fig. 9b. Although the heat values increased with the amount of coexisting electrolyte in both cases, the lithiated electrode coexisted with electrolyte generated less heat than that of the delithiated electrode (Fig. 9a). On the other hand, the differences of heat values were significant when the coexisting electrode increased from 1 to 3 mg, as shown in Fig. 9b. For the mixture of lithiated electrode and electrolyte, the heat value gradually decreased with the increasing of the lithiated electrode. In contrast, a fluctuation of heat value was observed for the delithiated electrode with electrolyte. Obviously, the heat generation from the mixtures of lithiated electrode and electrolyte was also smaller than that of delithiated electrode. Consequently, it is reasonable to state that the lithiated FeF<sub>3</sub> electrode showed better thermal stability than delithiated FeF<sub>3</sub> electrode in the MFA-based electrolyte.

The thermal behaviors can be affected by many factors such as active materials, electrolyte and binder. Thus, the FeF<sub>3</sub> cathodes in MFA-based electrolyte exhibited different thermal behaviors from that in EC + DMC-based electrolyte as previously reported [3]. For the mixtures of delithiated electrode and MFA-based electrolyte, the heat generation from the mixtures was observed at about 480 °C, which was about 230 °C higher than that of EC + DMC-based electrolyte [3]. On the other hand, the mixtures of lithiated electrode and MFA-based electrolyte showed the exothermic peaks

at temperatures above 350 °C, which was 140 °C higher than that of EC + DMC-based electrolyte [3]. However, the heat values of both the lithiated and delithiated FeF<sub>3</sub> electrodes in MFA-based was larger than that related to EC + DMC-based electrolyte. Although the heat release of the cycled electrodes in MFA-based electrolyte was larger, the exothermic reactions in MFA-based electrolyte occurred at much higher temperatures. Therefore, the safety of FeF<sub>3</sub> battery was improved by using MFA-based electrolyte instead of EC + DMC-based electrolyte.

#### 4. Conclusions

The thermal behaviors of a FeF<sub>3</sub> electrode in MFA-based electrolyte were quantitatively studied by DSC. DSC measurements revealed that MFA-based electrolyte containing LiPF<sub>6</sub> exhibits great thermal stability up to 500 °C. The thermal behaviors of the cycled FeF<sub>3</sub> electrodes were quite similar to that of the electrodes obtained for EC + DMC-based electrolyte, indicating that similar lithiation/delithiation reactions occurred for FeF<sub>3</sub> electrodes. To clarify the factor contributing to thermal risk, thermal behaviors of the mixtures of cycled electrode and electrolyte were investigated in detail by changing the ration of cycled electrode to electrolyte. For the mixtures of lithiated electrode and electrolyte, the thermal behavior was much more complicated. At least three reactions were involved in the mixture of lithiated electrode and electrolyte at elevated temperatures, including (a) self-decomposition of electrode, (b) the reaction between the electrode and electrolyte, (c) thermal reaction between the electrolyte and the products of the reaction between the electrode and electrolyte. For the mixtures of delithiated electrode and electrolyte, the exothermic heat was mainly attributed to the reaction of FeF<sub>3</sub> and electrolyte, while the irreversible LiFeF<sub>3</sub> in delithiated electrode also released some heat by reacting with the electrolyte. By comparing the heat values of lithiated/delithiated electrodes in MFA-based electrolyte, the lithiated FeF<sub>3</sub> electrode showed a superior thermal stability in MFA-based electrolyte. Simultaneously, the thermal behaviors of cycled FeF<sub>3</sub> cathodes in MFA-based and EC + DMC-based electrolytes were compared. Although the heat generated by the mixture of cycled FeF<sub>3</sub> electrodes and MFA-based electrolyte was larger, the delithiated and lithiated electrodes coexisted with MFA-based electrolyte were about 230 and 140 °C higher than that of EC + DMC-based electrolyte, respectively. Therefore, the safety of FeF<sub>3</sub> battery was enhanced by using MFA-based electrolyte instead of EC + DMC-based electrolyte.

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